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Measurements of Volatile Organic Compound Concentrations in Kraft Pulp and Paper Mill Streams

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ABSTRACT

The present study successfully demonstrated the measurements of the concentrations of volatile organic compounds (VOCs), i.e., methanol, methyl ethyl ketone (MEK), and acetone, in various pulp and paper mill streams using a commercial headspace gas chromatographic (HSGC) system. An indirect HSGC method reported in the literature was employed to conduct the present study. The study indicates that methanol and MEK or acetone concentration as high as 10,000 and 1,000 mg/L, respectively, can be measured with the present approach. With the headspace and GC conditions used in the present study, it was found that good separation of various substances present in pulp and paper mill streams can be achieved. Validation of the present study were achieved using VOC-water mixtures of known concentrations as well as using pulp and paper mill streams by multiple standard addition HSGC method. Mathematical precision analysis and experimental verifications indicated that the present measurements are accurate and repeatable. The VOC concentration data in various pulp and paper mill streams obtained in this study provides an important reference for the pulp and paper industry.

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INTRODUCTION

Volatile organic compounds (VOCs) in pulp and paper mill streams has been an environmental concern. These VOCs are soluble in water and become an important source of biodegradable organic compounds to increase the biochemical oxygen demand (BOD). Furthermore, these species can also be released into the atmosphere at the process temperatures of kraft mill streams. The new toxic and permit provisions of the 1990 Clean Air Act Amendments require information on emissions of volatile organic compounds (VOCs) from pulp and paper mill sources. Many pulp and paper mills are required to report VOC emisison data for permit applications for changing operating processes. Therefore, computer models [1-3] that can predict VOC emissions provide a tool for mills to control VOC emissions in changing processes. As indicated by a recent mill emission study [4] conducted by the National Council for Air and Stream Improvement (NCASI), the emission of VOCs in kraft mills depends mainly on (1) the VOC content in mill streams, (2) the fundamental thermodynamic vapor-liquid phase equilibrium behavior of the VOCs in mill streams, (3) the mass transfer associated with specific mill processes, and (4) the mill operating conditions, such as wood species, pulping chemicals used, water reuse in operation, etc. Therefore, developing a database of VOC concentrations in various pulp and paper mill streams is very important for BOD control and accurate emission predictions using computer models.

It is not trivial to analyze samples from various mill streams using conventional direct analytical methods with delicate laboratory instruments through calibration because some of the mill streams are corrosive in nature. Gunshesfki and Cloutier [5] developed a method to measure methanol (MeOH) concentration in black liquor (a spent liquor from wood pulping). However, their method modifies the sample matrix through the addition of chemicals to precipitate the solids in weak black liquors. The method has several disadvantages: (1) the amount of chemicals added (mass ratio of chemical over black liquor = 30:1) significantly dilutes the VOC concentration in the sample and reduces the measurement accuracy; (2) the method is only suitable for the analysis of weak black liquors as the solid precipitation method may not be used for other mill streams; and (3) the method is tedious and time consuming.

Headspace gas chromatography (HSGC) provides direct analysis of the vapor phase of a solute in any sample matrix. Many HSGC techniques have been developed for quantitative

analysis of solute concentration in samples through the analysis of the solute in the vapor phase. Therefore, HSGC is very suitable for the analysis of VOCs in samples such as those collected from pulp and paper mills that are corrosive and may containing particles or fiber suspensions. These HSGC techniques, including direct analysis that requires calibration and indirect analysis that does not require calibration, have been described in several review articles [6,7] and books [8,9]. The objective of the present study is to demonstrate one HSGC method developed by Drozd and Novak [10] for quantitative analysis of VOCs, i.e., methanol, MEK, and acetone concentrations in kraft pulp and paper mill streams.

METHODOLOGY

The derivation of the indirect HSGC method used in the present study can be found in the work of Drozd and Novak [10]. It is based on the thermodynamic vapor-liquid phase equilibrium of the solute under analysis as mentioned in the literature. To demonstrate the method for VOC concentration measurements in kraft pulp and paper mill streams, we describe the method schematically as shown in Fig. 1. We used two sample vials, both filled with the same amount of sample solution. Then, we add a known small amount of concentrated solution into one of the vials. The volume of the solution added is very small compared with the volume of the original solution and, therefore, can be neglected. We conduct headspace GC analysis of each sample after phase equilibrium was established within each vial. We can assume that the solute concentrations in these two sample vials are still very low or the solute concentrations are under infinite dilution (which is valid for most VOCs in mill streams even after the standard addition). Therefore, the solute VLE partitioning in these two vials follows the Henry's Law, which connects the two independent headspace measurements to determine the solute content in the original sample. According to Drozd and Novak [10], the mathematical expression of the technique described in Fig.1 can be expressed as follows,

$$C_0 = \frac{C_S V_S}{\left(C_{G2} / C_{G1} - 1\right) \cdot V_{L0}} \qquad (1)$$

where, C_0 is the concentration of the solute to be measured, V_{L0} is the initial sample volume in the testing vial, V_S and C_S are the volume and solute concentration of the solution that is spiked (added into the testing vial) through standard addition, and C_{G2} / C_{G1} is the ratio of the solute

concentration in the vapor that is proportional to the ratio r_A of the peak areas A_2 and A_1 of the two HSGC measurements. We can rewrite Eqn. (1) as,

$$C_0 = \frac{C_S V_S}{(A_2 / A_1 - 1) \cdot V_{L0}} = \frac{C_S V_S}{(r_A - 1) \cdot V_{L0}} \qquad (2)$$

Eqn. (2) was used to determine the VOC concentrations in various mill streams in this study.

EXPERIMENTAL

Chemicals

We used methanol, methyl ethyl ketone (MEK), and acetone to mix with deionized water to make standard solutions of methanol-water, MEK-water, and acetone-water to validate the present methods.

We conducted measurements of VOC concentrations and VLE partitioning in various mill streams from four separate kraft mills (Mills A, B, C, and D) to demonstrate the applicability of the present methods.

Apparatus and Operation

All measurements were carried out using an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph (Hewlett-Packard). GC conditions: capillary column (Hewlett-Packard, HP-5, 30 meters long) at 30°C; carrier gas helium flow (He): 3.8 mL/min. A flame ionization detector (FID) was employed with hydrogen and air flows of 35 and 400 mL/min, respectively. Headspace operating conditions: 25 minutes gentle shaking for equilibration of the sample, vial pressurization time: 0.2 min, sample loop fill time: 1.0 min., and loop equilibration time: 0.05 min.

Temperature of the Headspace Sampler

For VOC concentration measurements, we set the temperature of the headspace sampler at 70°C to avoid water vaporization and obtained a good sensitivity as sufficient methanol is present in the vapor phase at this temperature.

Chromatographic Separation of Various Compounds

Samples from pulp and paper mill streams consist of various compounds that can be present in the vapor phase at the headspace temperature used in this investigation. Accurate measurement of the concentration of each VOC species requires good separation of the signals from each species without interference during chromatography. Weak black liquor and filtrate from brown stock washing (the process that washes away pulping dissolved wood lignin from wood fibers) contain a very small amount of methyl mercaptan. A GC column temperature of 30°C is used to separate the signal of methyl mercaptan from the methanol signal. Because the concentration of methyl mercaptan is much lower than that of methanol, the signal separation obtained as shown in Figs. 2a and 2b using the GC conditions described above is sufficient to achieve the accuracy for the present study. A better seperation of methyl mercaptan from methanol can be obtained using a longer column (60 meters) at sub-ambient temperature. Fig. 2 also shows the chromatograms obtained from other pulp and paper mill samples, i.e., 2c is a chromatogram from an oxygen delignification (a process to further delignin in fibers through reaction with molecular oxygen in alkaline medium at high pressure) washing filtrate and 2d is from D_o bleaching (a fiber bleaching process through the reaction with chlorine dioxide) vat liquor. Good separations of methanol, MEK and acetone from other substances were obtained. We would like to point out that the present study is only interested in the measurements of methanol, MEK, and acetone. Sulfur compound VOCs such as methyl mercaptan and dimethyl sulfide produced in kraft pulp mills are responsible for kraft mill odor problem, and therefore, deserve more detailed study in the future. Furthermore, sulfur compound VOCs are only observed in the pulp mill streams, such as black liquor, brown stock washer filtrate, etc., and are not present in paper mill streams, such as paper machine white water, filtrates from bleaching stages, etc.

RESULTS AND DISCUSSION

Precision Analysis of the Method

Although the present method was developed in the 1970s, detailed mathematical analysis of the precision of the present method has not been conducted. The ratio of the substance spiked (added) to that native present in the sample is the only parameter that can be adjusted in the

application of the present HSGC method. We conducted a mathematical precision analysis of Eqn. (7) using the following variance estimation equation:

$$\sigma^2(C_0) = \left(\frac{\partial C_0}{\partial C_S}\right)^2 \sigma^2(C_S) + \left(\frac{\partial C_0}{\partial V_S}\right)^2 \sigma^2(V_S) + \left(\frac{\partial C_0}{\partial V_{L0}}\right)^2 \sigma^2(V_{L0}) + \left(\frac{\partial C_0}{\partial r_A}\right)^2 \sigma^2(r_A) \qquad (3)$$

where the partial derivatives can be calculated using Eqn. (2). The variance of r_A can be calculated from the variance of peak area A_1 and A_2, similar to that of C_0,

$$\sigma^2(r_A) = \frac{A_2^2}{A_1^4}\sigma^2(A_1) + \frac{1}{A_1^2}\sigma^2(A_2) \qquad (4)$$

We conducted replica HSGC measurements [11] in nine testing vials filled with 10 μL (much less than the 10 mL sample volume used in the present study) of methanol-water mixture with methanol concentration of 800 mg/L to determine the variance of the GC peak area A. We found that the relative standard deviation of the nine measurements was 2.1%. Based on this experiment, we take $\sigma^2(A_1) = (2.5\%A_1)^2$, and $\sigma^2(A_2) = (2.5\%A_2)^2$. We have $\sigma^2(r_A) = 1.25\text{x}10^{-4}.(r_A)^2$ from Eqn. (4). The variances of other independent variables were also determined experimentally. We found from experiments that the main contribution to the variance of C_0 is the r_A term. By neglecting the contribution from other measurable experimental variables with the substitution of r_A using Eqn. (2), we have

$$\sigma^2(C_0) \approx 1.25\times10^{-4} \cdot \left(\frac{V_S}{V_{L0}}\right)^2 \cdot \left[\frac{\frac{C_S V_S}{C_0 V_{L0}} + 1}{\frac{C_S V_S}{C_0 V_{L0}}}\right]^2 = 1.25\times10^{-4} \cdot \left(\frac{V_S}{V_{L0}}\right)^2 \cdot \left[\frac{Y+1}{Y}\right]^2 \qquad (5)$$

where Y is the ratio of substance spiked over that native present in the sample. V_S is assumed negligible compared to V_{L0} in deriving Eqn. (2). In the present study the ratio of V_S over V_{L0} was taken 0.001. Therefore, Y is an experimental variable that can be used to optimize the accuracy of the present method using Eqn. (2).

Mathematical calculations were carried out to study the effect of substance ratio Y on the accuracy of the method as shown in Fig. 3. The symbols are the experimentally determined the measurement uncertainties using methanol, MEK, and acetone-water solutions with known concentration ranges of 150-1600, 8-40, and 1-5 mg/L, correspondingly. The results indicate

that a substance ratio Y = 0.2 is sufficient to obtain good measurements (error < 10%) of VOCs in the concentration ranges given. The results also indicate that all the experimentally determined uncertainties are within the prediction limit, indicating that the assumed error in the peak area of 2.5%A (or the peak area ratio of $\sqrt{1.25} \times 10^{-2} r_A$) is arger than the actual experimental error.

Technique Validation

Using VOC-Water Solutions

The method has been validated by Drozd and Navak [10] using acetone-, methanol-, ethanol-, and propanol-water solutions with solute concentration ranges of 1-100, 2-6, 3-10, and 1-4 mg/L, correspondingly. Because the concentrations of methanol, MEK or acetone in kraft mill streams can be as high as on the order of thousands, and tens mg/L, respectively, we conducted a set of experiments to validate the applicability of the method using a set of standard VOC-water (methanol-, MEK-, and acetone-water) solutions with concentrations of 100-2000, 10-100, and 1-10 mg/L, respectively. The combined concentration range covers trace species concentration over three orders of magnitude. The comparison between the standard and the measured data is excellent as shown in Fig. 4. To demonstrate the validity of the Henry's Law in the concentration range studied, which is the basic assumption of the method, we measured the Henry's Law constants in a set of VOC-water (methanol-, MEK-, and acetone-water) solutions using the method we developed [11] with concentration ranges shown in Fig. 4. We found that Henry's constant for methanol is essentially a constant as shown in Table I. The standard deviation of the 10 measurements was only 4.2%. Similar results were also obtained for MEK and acetone in the concentration range shown in Fig. 4.

We conducted a set of HSGC measurements to study the effect of VOC concentration on the response of the GC detector to further demonstrate the validity of the measurements presented in this study. A nonlinear response can occur if too much solute were transferred into the GC column causing incomplete combustion or saturation of the detector. We call this type of nonlinear response the instrument or experimental condition-related nonlinearity. A nonlinear response can also occur when the Henry's Law is invalid. We call this type of nonlinear response the vapor-liquid equilibrium (VLE) nonlinearity because it is caused by the thermodynamic behavior of the solution system under investigation. The instrument nonlinearity

can be adjusted through optimization of GC conditions, headspace conditions, sample size, etc. The VLE nonlinearity cannot be improved and poses the upper concentration limit on the present method. The objective of the present study is not to establish the upper concentration limit of the present indirect HSGC method for VOC concentration measurements, rather to demonstrate the method for VOC measurements in pulp and paper mill streams. Therefore, we use the concentration ranges of the VOCs in the pulp and paper mill streams in establishing the instrument and experimental conditions. The GC detector responses shown in Fig. 5 were obtained under established instrument and experimental conditions described in the previous section. Fig. 5 indicates that the present method is applicable to measure methanol, MEK or acetone concentration as high as 20,000 and 1,000 mg/L at 70°C with a 11.6 mL headspace volume and 10 mL liquid sample size, respectively. Because standard addition is used in this study, the actual amount of VOCs in the sample solution can be measured will be reduced by the amount substance spiked.

We also conducted 10 replica measurements of a methanol-water solution with concentration 400 mg/L to demonstrate the repeatability of the present method. The results are listed in Table II. The relative standard deviation of the measurements was only 4.2%.

Using Samples from Pulp and Paper Mills

The objective of the present study is to demonstrate that the present indirect HSGC method [10] can be applied to measure VOC concentrations in pulp and paper mill streams. As we discussed previously, there are limited analytical methods available for accurate quantitative analysis of VOCs in these streams. The validation of the present measurements in pulp and paper mill samples was achieved by extrapolating the GC headspace measurement results from multiple standard addition experiments as described by Kolb and Ettre [9]. Fig. 6 shows the results from a typical multiple standard addition experiment using a first-stage brown stock washer filtrate sample. Brown stock washing in pulp mills is the process that is not enclosed and therefore during which methanol can be released into the atmosphere. The filtrate sample contains pulping dissolved wood lignin, other organic and inorganic solid particles, and may be some very fine fiber suspensions, therefore direct GC injection measurements of this sample is difficult. In Fig. 6, the x coordinate is the amount of standard methanol added into the filtrate sample, the y coordinate is the measured GC peak area of the headspace vapor after each

addition. Because the Henry's constant is remained unchanged after each standard addition (the solution is still considered infinitely diluted within the concentration range under investigation), a linear response,

$$A = a + b \cdot m, \qquad (6)$$

as shown in Fig. 6 is expected. The amount of methanol native present in the original sample is nothing but the negative value of the intercept of the line on the x coordinate, or,

$$m_0 = m_{A=0} = \left| a/b \right| \qquad (7)$$

The concentration of the original sample can be calculated,

$$C_0 = m_0 / V_{L0} = \frac{\left| a/b \right|}{V_{LO}}. \qquad (8)$$

For the data shown in Fig. 6, we found that the methanol concentration in the brown-stock washing filtrate sample is 260 mg/L according to Eqn. (8). We conducted the above described validation experiment for several samples from various pulp and paper mill streams. These samples provide a good representation of streams from various pulp and paper manufacturing processes such as pulping (weak black liquor is a spent liquor from pulping), washing, oxygen delignification, bleaching, paper making, etc. The pH levels of these samples vary from 2.3 to 12.2. We compared the methanol concentrations in these samples obtained from Eqn. (8) with those measured by the indirect HSGC method by Drozd and Novak through Eqn. (2) to validate the present study. Good agreements between these two methods were obtained as listed in Table III, indicating the validity of the present study.

We also conducted repeatability studies using Eqn. (2) to demonstrate the uncertainty of the present study. Weak black liquor and filtrate stream from the first brown stock washer were chosen to conduct the study because these two samples deviate the most from aqueous solution and are therefore the most difficult to analyze. The inorganic and organic solids contents of these two samples are 11.5 and 1.65%, respectively. As listed in Table IV, the results indicate that standard deviation of the replica measurements are less than 2%, well within the predicted measurement uncertainty limits shown in Fig. 3.

Comparison with NCASI Method

To further demonstrate the validity of the present study, we compared the measurements of methanol concentrations in four weak black liquor samples from two pulp mills using the present described method (Eqn. (2)) with those obtained by NCASI's method [5]. Again, excellent agreement were obtained as listed in Table V. The differences are within the measurement uncertainties of the two methods.

Measurements in Various Mill Streams

We measured methanol and MEK concentrations in various kraft mill streams from Mill C using the present method. The results are shown in Table VI. Mill C is an unbleached kraft paper mill. For this particular mill, the data indicate: (1) the weak wash stream in the recovery cycle does not contain methanol; (2) the shower water and filtrate streams in the washers contain a significant amount of methanol; (3) the blow tank condensate stream from the digester also has a high content of methanol as indicated by the measurement of the sample from the hot water tank; (4) the white water from the paper-machine head tank for the present unbleached mill contains some methanol; (5) weak black liquor has a significant amount of methanol; and (6) MEK concentrations in various streams are in the order of a several hundred of ppb, and they do not have a direct correlation with the concentrations of methanol. Similar conclusions can be drawn from the measurements of VOC concentrations of various streams in another unbleached Mill D as shown in Table VII . The absolute concentrations of VOCs in mill streams depend on various factors such as water dilution, mill operating conditions, and VOC formation.

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Fig. 1

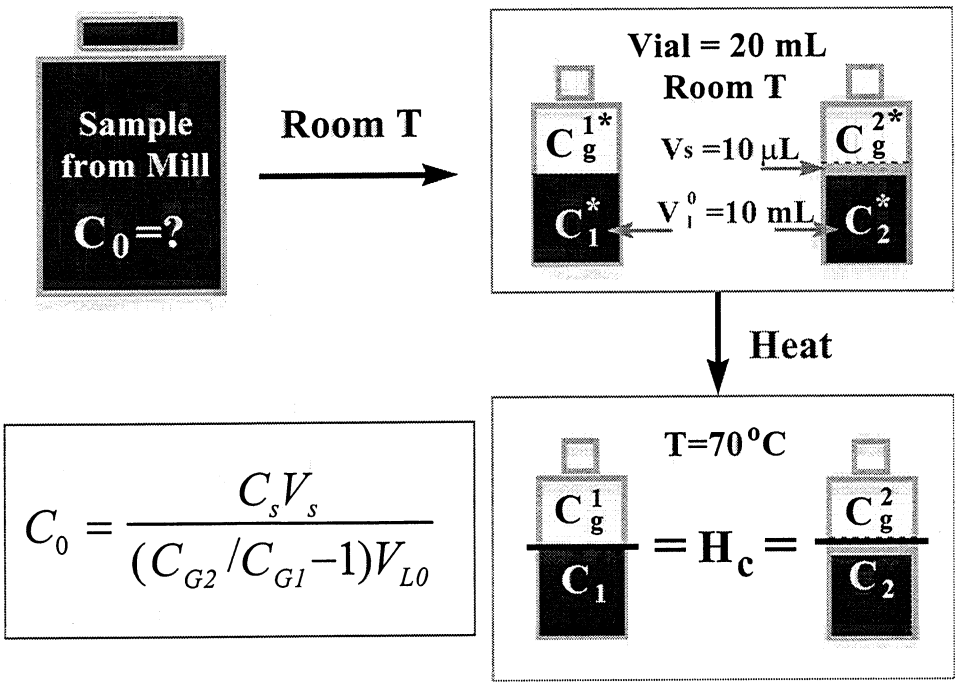
Sample from Mill
C_0=?
Room T
Vial = 20 mL
Room T
C_g^{1*}
C_1^*
Vs =10 μL
V_1^0 =10 mL
C_g^{2*}
C_2^*
Heat
T=70°C
C_g^1
C_1
$= H_c =$
C_g^2
C_2
$C_0 = \frac{C_s V_s}{(C_{G2}/C_{G1} - 1)V_{L0}}$

Fig. 2

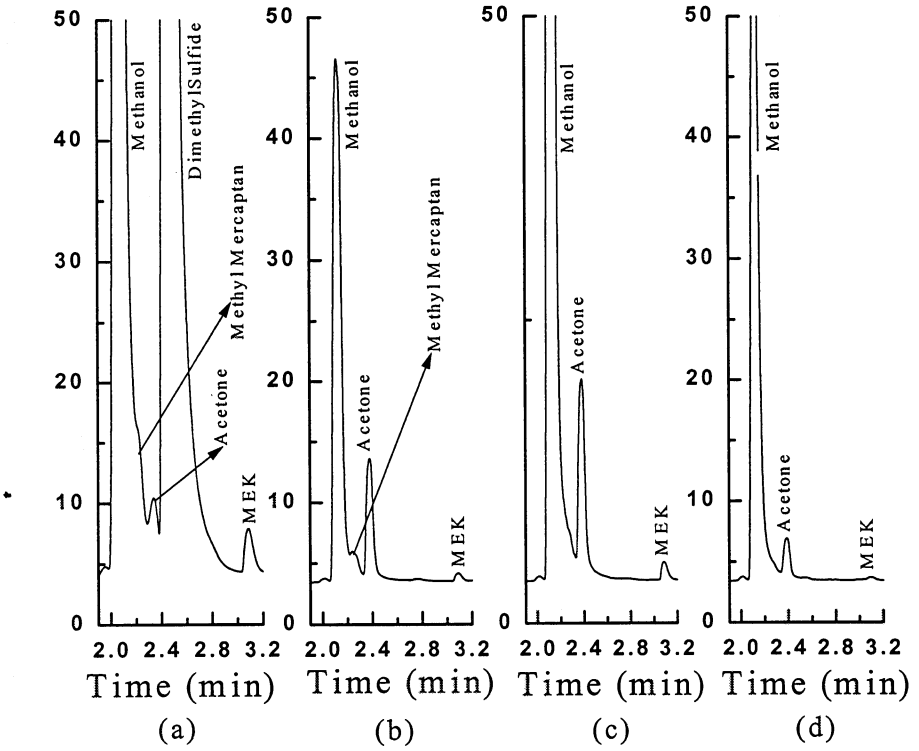
Methanol
Dimethyl Sulfide
Methyl Mercaptan
Acetone
MEK
Time (min)
(a)
(b)
(c)
(d)

Fig. 3

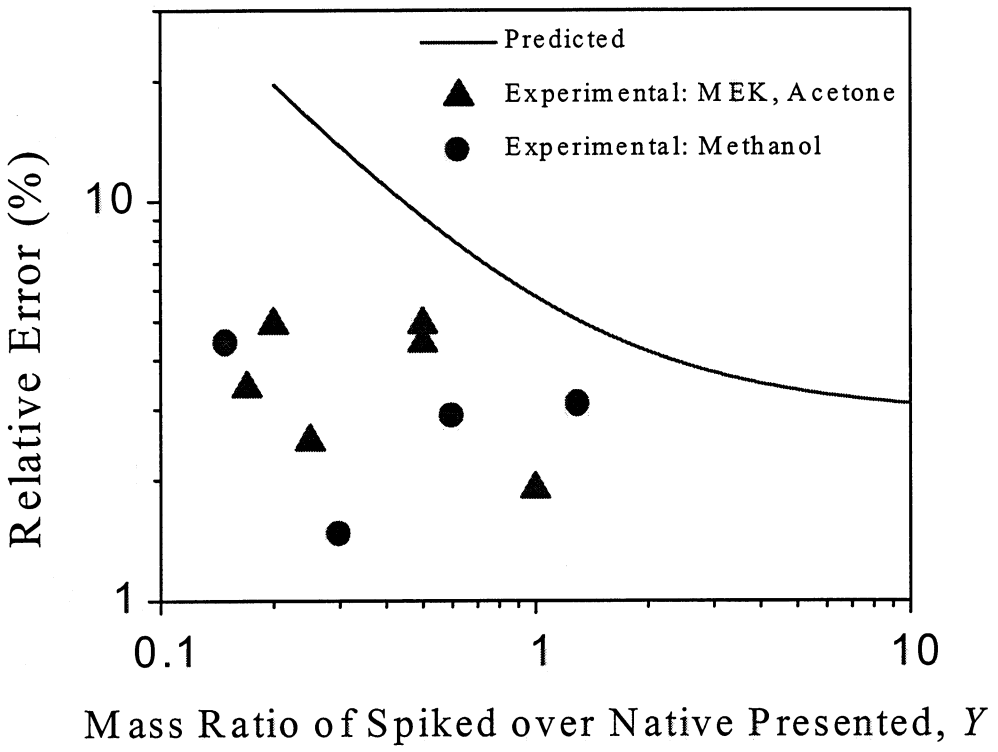
Predicted
Experimental: MEK, Acetone
Experimental: Methanol
Relative Error (%)
10
1
0.1
1
10
Mass Ratio of Spiked over Native Presented, Y

Fig. 4

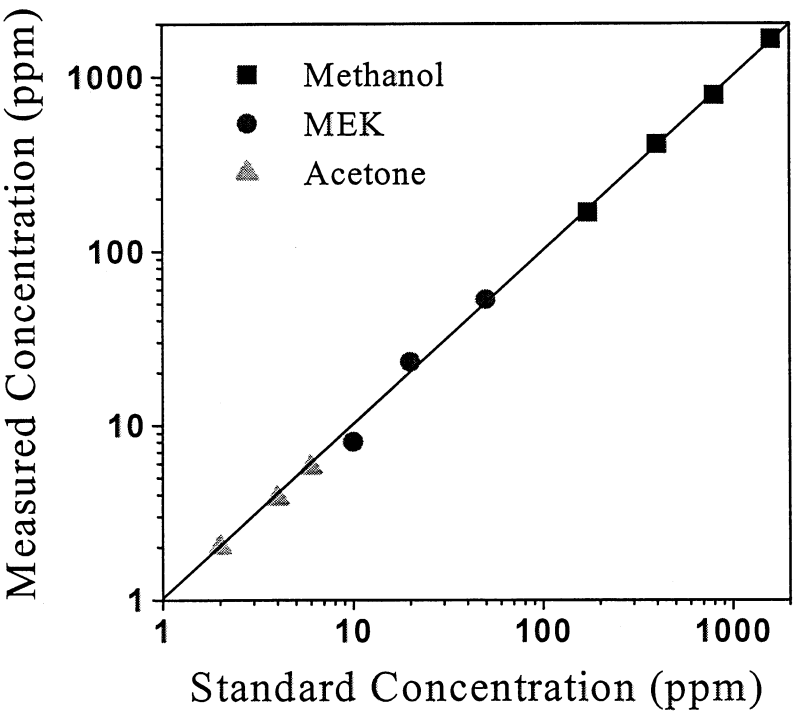
Methanol
MEK
Acetone
Measured Concentration (ppm)
1000
100
10
1
1
10
100
1000
Standard Concentration (ppm)

Fig. 5

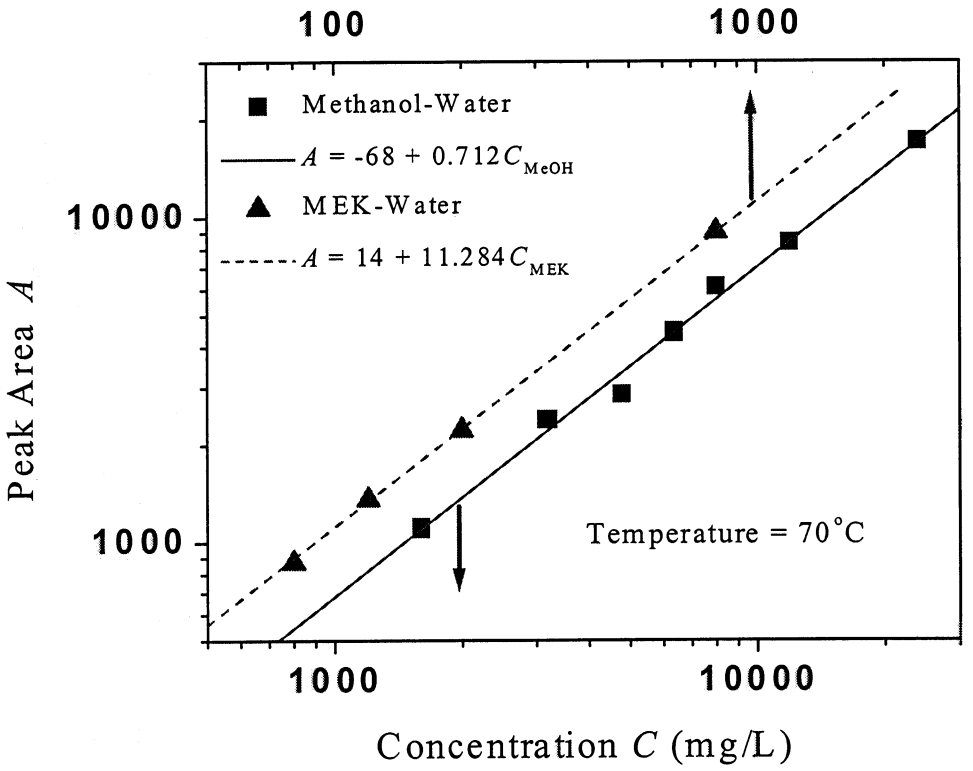
100
1000
Methanol-Water
$A = -68 + 0.712C_{MeOH}$
MEK-Water
$A = 14 + 11.284C_{MEK}$
10000
1000
Peak Area A
Temperature = 70°C
1000
10000
Concentration C (mg/L)

Fig. 6

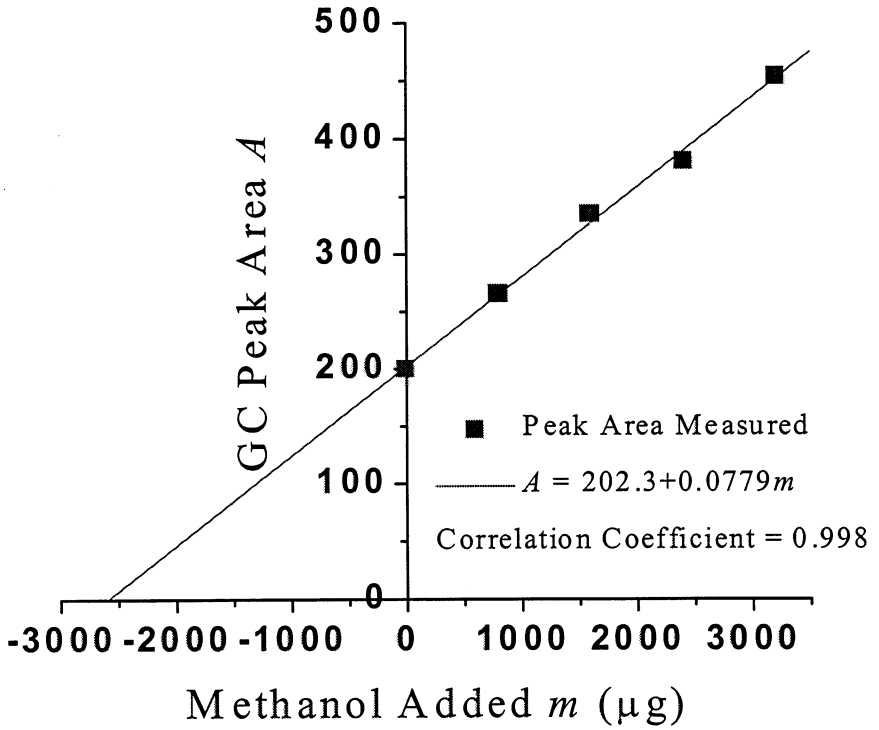
500
400
300
200
100
0
GC Peak Area A
Peak Area Measured
$A = 202.3+0.0779m$
Correlation Coefficient = 0.998
-3000 -2000 -1000 0 1000 2000 3000
Methanol Added m (μg)

Table I. Measured Henry's Law constant of methanol in water solutions at various concentrations

Concentration (mg/L)	Henry's Constant
2000	0.00172
1600	0.00184
1200	0.00169
800	0.00187
480	0.00174
400	0.00172
342	0.00170
300	0.00172
200	0.00165
100	0.00180
Mean	**0.00175**
Relative STD	**4.2%**

Table II. Replica measurements of methanol concentration in a water mixture of given concentration 400 mg/L

Experiment	Measured Concentration (mg/L)
1	397
2	430
3	375
4	409
5	405
6	403
7	404
8	423
9	389
10	425
MEAN	**406**
Error	**1.5%**
Relative RSD	**4.2%**

Table III. Comparisons of methanol concentrations in several pulp and paper mill streams measured by the present indirect HSGC method and a multiple standard addition HSGC method.

Sample Description	pH	Indirect HSGC Method [10] Eqn. (2)	Multiple Standard Addition Eqn. (8)	Difference (%)
Brown Stock Washer Filtrate	11.7	251	260	-3.5
Brown Stock Washer Shower	11.0	277	284	-2.5
Weak Black Liquor	9	447	465	-3.9
Oxygen Delignification Diffusion Washer Filtrate	10.9	935	905	3.3
D_0 Bleaching Stage Vat Liquor	2.3	351	364	-3.6
E_2 Bleaching Stage Filtrate	12.0	53	51	3.9
Paper Machine White Water	7	40	40	0

Table IV Replica measurements of methanol concentration in black liquor and MEK concentration in brown stock washer filtrate.

Experiment	Methanol Concentration in Black Liquor (mg/L)	MEK Concentration in Washer Filtrate (μg/L)
1	592	409
2	604	404
3	605	404
4	586	416
5	600	408
6	599	401
7	602	404
8	599	405
9	606	-
10	610	-
MEAN	**601**	**406**
Relative RSD	**1.2%**	**1.1%**

Table V. Comparisons of measured liquid methanol content in four black liquors using the NCASI method and the present method.

SAMPLE	Solids Content (%)	Methanol Concentration (mg/L)		
		NCASI Method	Present Method	Difference (%)
Softwood, Mill A	15.2	775	736	-5.0
Hardwood, Mill A	17.1	961	906	-5.7
Softwood, Mill B	11.5	434	447	3.0
Hardwood, Mill B	10.8	527	560	6.3

Table VI. Methanol and MEK concentrations measured in various streams from Mill C.

Sample Number	Sample Location Description	Methanol (ppm)	MEK (ppb)
1	weak wash liquor from recovery cycle	0	74.5
2	white water from paper-machine head tank	40	0
3	pulp wash shower water first stage digester (D1)	277	165
4	filtrated stream from first washing stage (D1)	251	433
5	filtrated stream from second washing stage (D1)	238	316
6	filtrated stream from first washing stage (D2)	201	583
7	filtrated stream from second washing stage (D2)	172	481
8	condensated stream of blow tank steam in hot water tank	315	251
9	weak black liquor to evaporator	272	307

Table VII. VOC concentrations measured in various streams from Mill D.

Sample Location Description	Label	MeOH	Acetone	MEK
		(ppm)	(ppb)	(ppb)
1st stage showers, 2nd stage filtrate	No. 1 Washer	209.5	494	406
	No. 2 Washer	275.0	484	394
2nd stage showers, 1st stage filtrate	No. 1 Washer	149.8	980	439
	No. 2 Washer	312.7	852	511
3rd stage showers	No. 1 Washer	122.6	683	452
	No. 2 Washer	203.8	715	526
side combined condensate (blow recovery)	No. 1 Washer	178.6	1327	592
	No. 2 Washer	382.6	1113	774
1st stage filtrate	No. 2 Washer	349.0	520	270
3rd stage filtrate	No. 1 Washer	332.2	930	564
combined weak black liquor to recovery		292.4	670	315
evaporator seal tank condensate	No. 2 (M24-0542)	93.1	762	665
	No. 2 (24-0529)	673.1	4138	425
evaporator clean condensate	No. 3	2.0	-	31
	No. 3 (24-0509)	1.7	-	231
Evaporator	No. 2	27.1	-	218
evaporator seal tank	No. 1 (M24-0027)	3954.4	11	2706
combined condensate of hotwell	No. 3	659.1	16067	7826
paper-machine condensate	No. 1	3.3	-	59
	No. 2 & No. 3	3.5	-	124
top headbox	No. 1	57.4	323	108
	No. 2	55.3	260	129
base headbox	No. 1	88.8	433	167
	No. 2	64.9	315	158
headbox	No. 3	46.8	-	-
wire pit	No. 1	86.5	375	141
	No. 2	91.8	508	129
	No. 3	90.9	-	-
water reclaim sump	No. 1	13.0	192	62
vacuum dump	No. 2	20.6	-	-
side hill screen drain off	No. 3	65.7	-	-